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Ionic liquid technology for recovery and separation of rare earths

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Acknowledgments

- Bart Blanpain, Tom Van Gerven, Jan Fransaer
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iwt

EREAN

EU FP7 Marie-Curie Initial Training Network

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materials for a better life

eu Rare

57-71

sustainable exploitation

SEVENTH FRAMEWORK PROGRAMME

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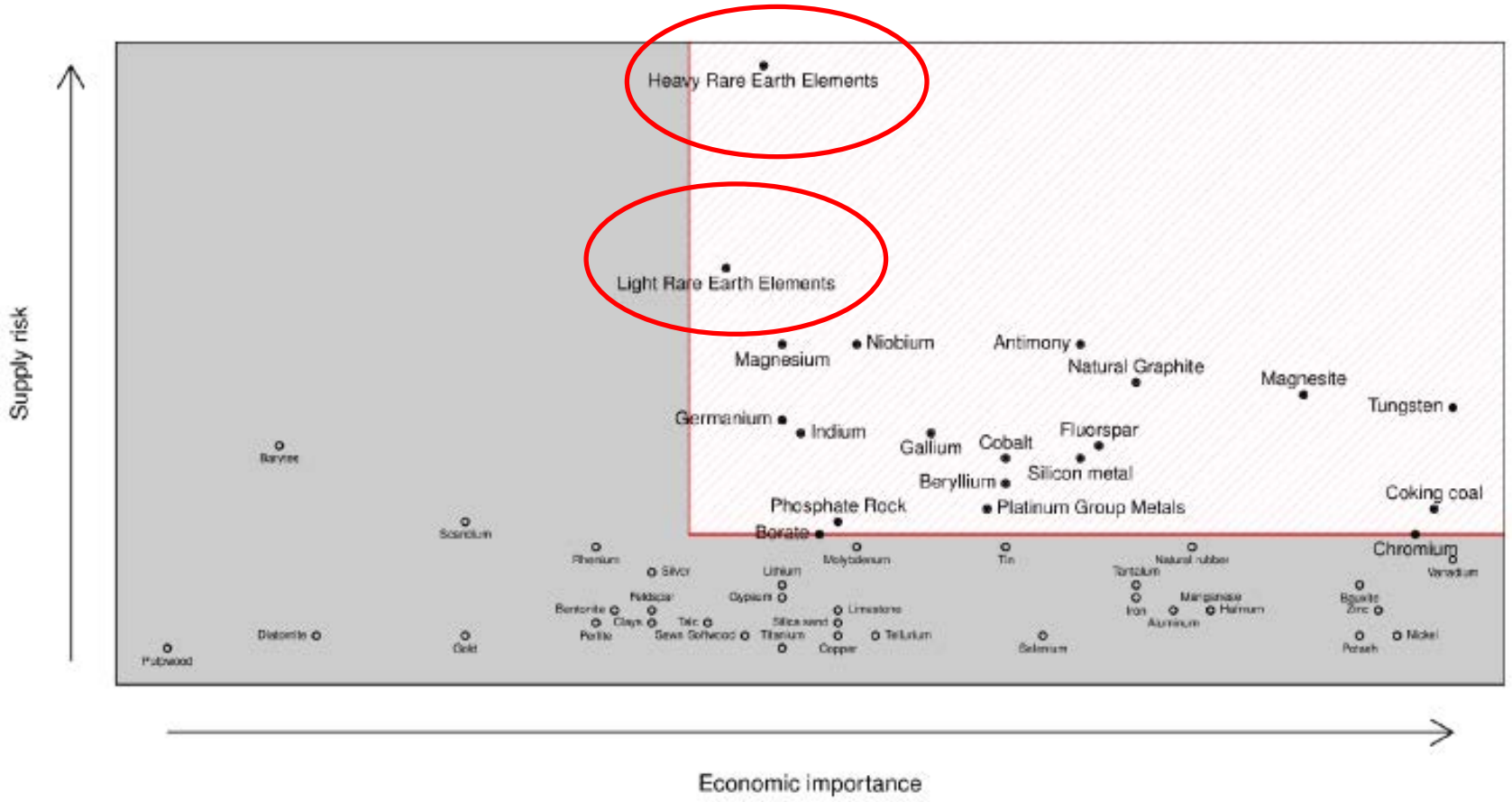
Rare earths as critical raw materials



Source: report EU commission “Critical raw materials for the EU” (2014)

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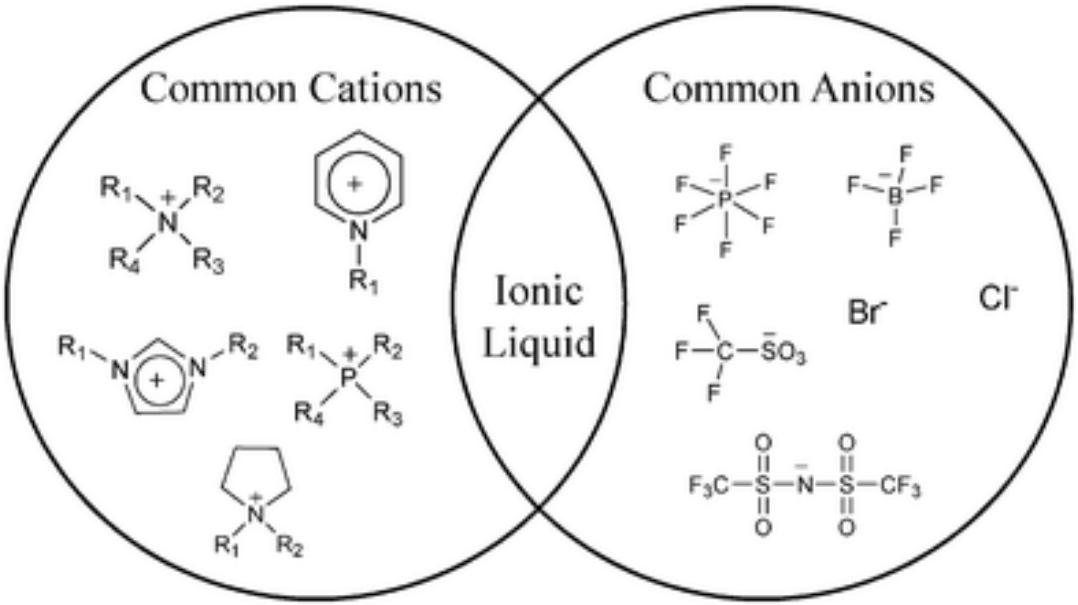
What are ionic liquids (ILs)?

- **Ionic liquids** are solvents that consist of cations and anions (opposite to molecular solvents and aqueous solutions)
- Low-melting organic salts (melting point < 100 °C)

  often liquid at room temperature



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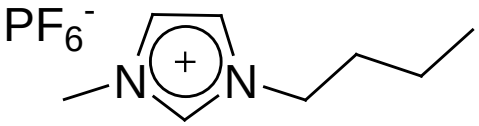
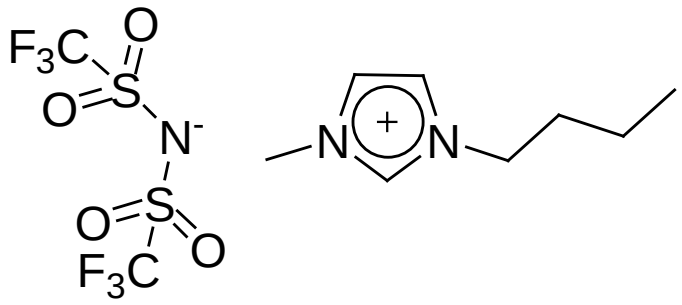
Ionic liquids in hydrometallurgy

- Organic phases in solvent extraction
  - Very low vapour pressure: non-volatile, non-flammable
    → safer extraction processes
  - Very high concentration of extractant (non-fluorinated ILs)
    → high metal loadings in organic phase
  - Other extraction mechanism compared to molecular systems
    → more selective extraction processes
- Lixiviant in leaching processes
    → smaller volumes, less waste water
    → leaching above 100 °C without use of autoclave

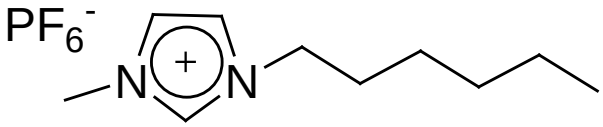
Ionic liquids with hydrophilic cations



[C_4mim][PF_6]



[C_4mim][Tf_2N]



[C_6mim][PF_6]

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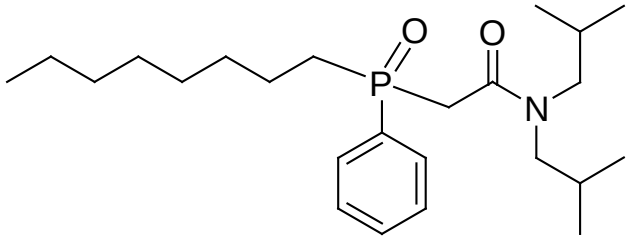
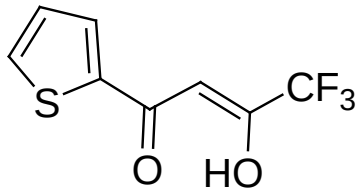
Losses of ionic liquid components

- Cation exchange mechanism



$$Ln^{3+}_{aq} + 3CMPO_{IL} + 3[C_nmim]^{+}_{IL} \leftrightarrows [Ln(CMPO)_3]^{3+} + 3[C_nmim]^{+}_{aq}$$

- Anion exchange mechanism



$$Ln^{3+}_{aq} + 4Htta_{IL} + [C_4mim][Tf_2N]_{IL} \leftrightarrows [C_4mim][Ln(tta)_4]_{IL} + 4H^{+}_{aq} + [Tf_2N]^{-}_{aq}$$

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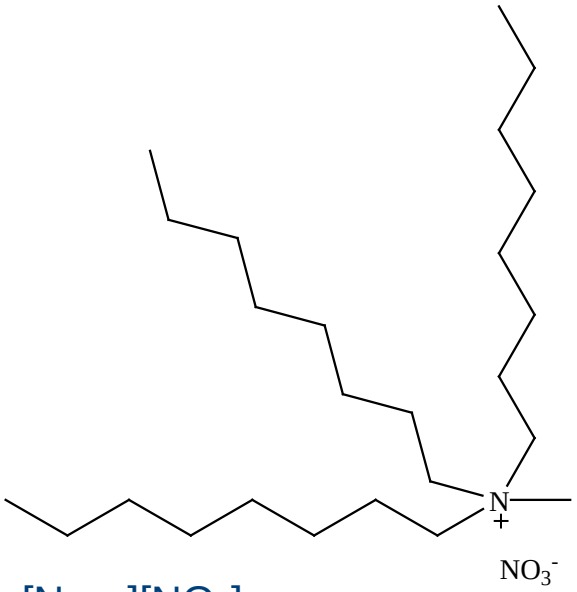
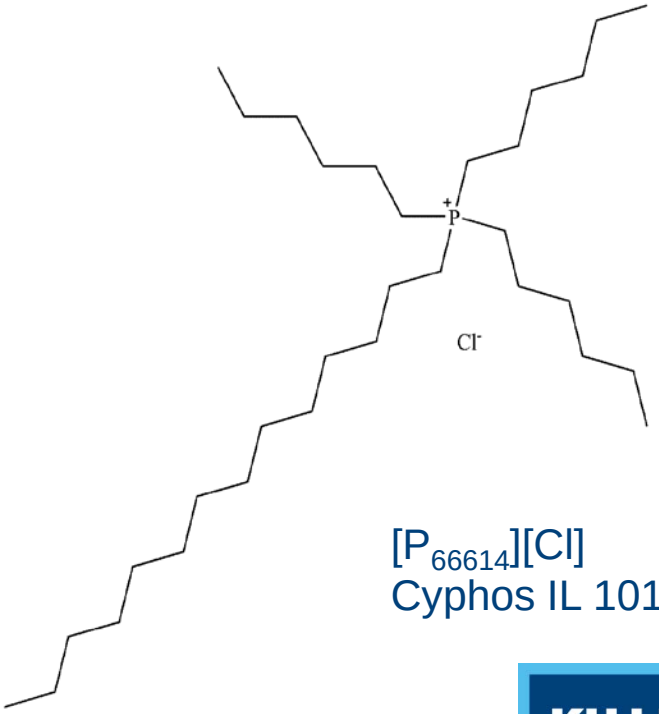
Approach at KU Leuven

- Focus on hydrophobic ILs with non-fluorinated anions (Cl^-, NO_3^-) → increasing chain length on cation makes IL hydrophobic
- No molecular organic solvents added



$[N_{8881}][NO_3]$
Aliquat 336 nitrate



$[P_{66614}][Cl]$
Cyphos IL 101

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Separation of rare earths by split-anion extraction

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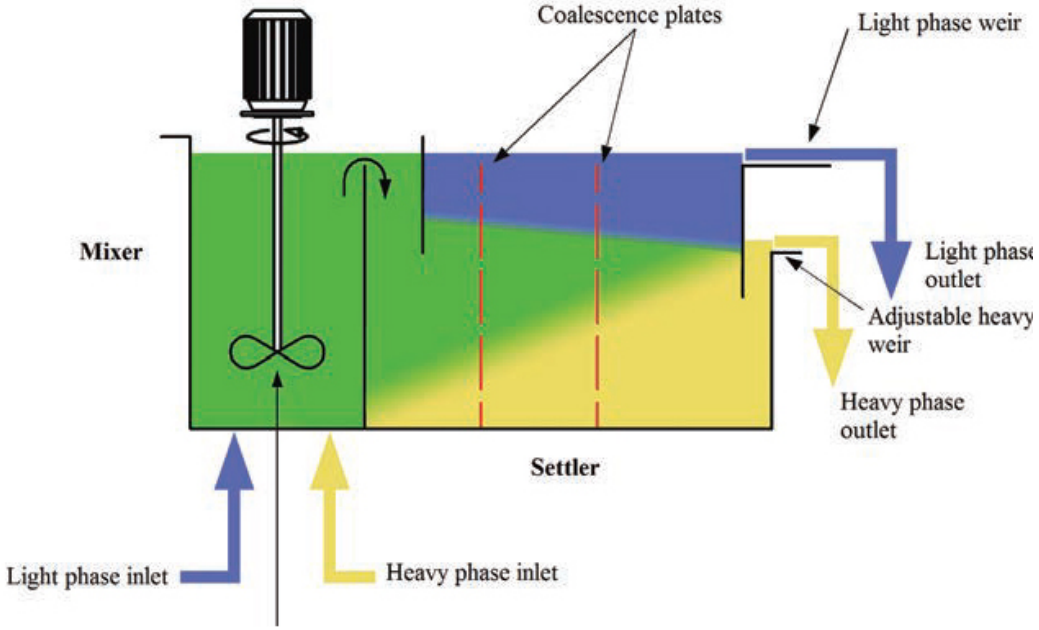
Separation of REEs

- Mixtures of REEs are separated on an industrial scale by solvent extraction (SX) in mixer-settlers



Source: Wikipedia

Distribution ratio/ Separation factor

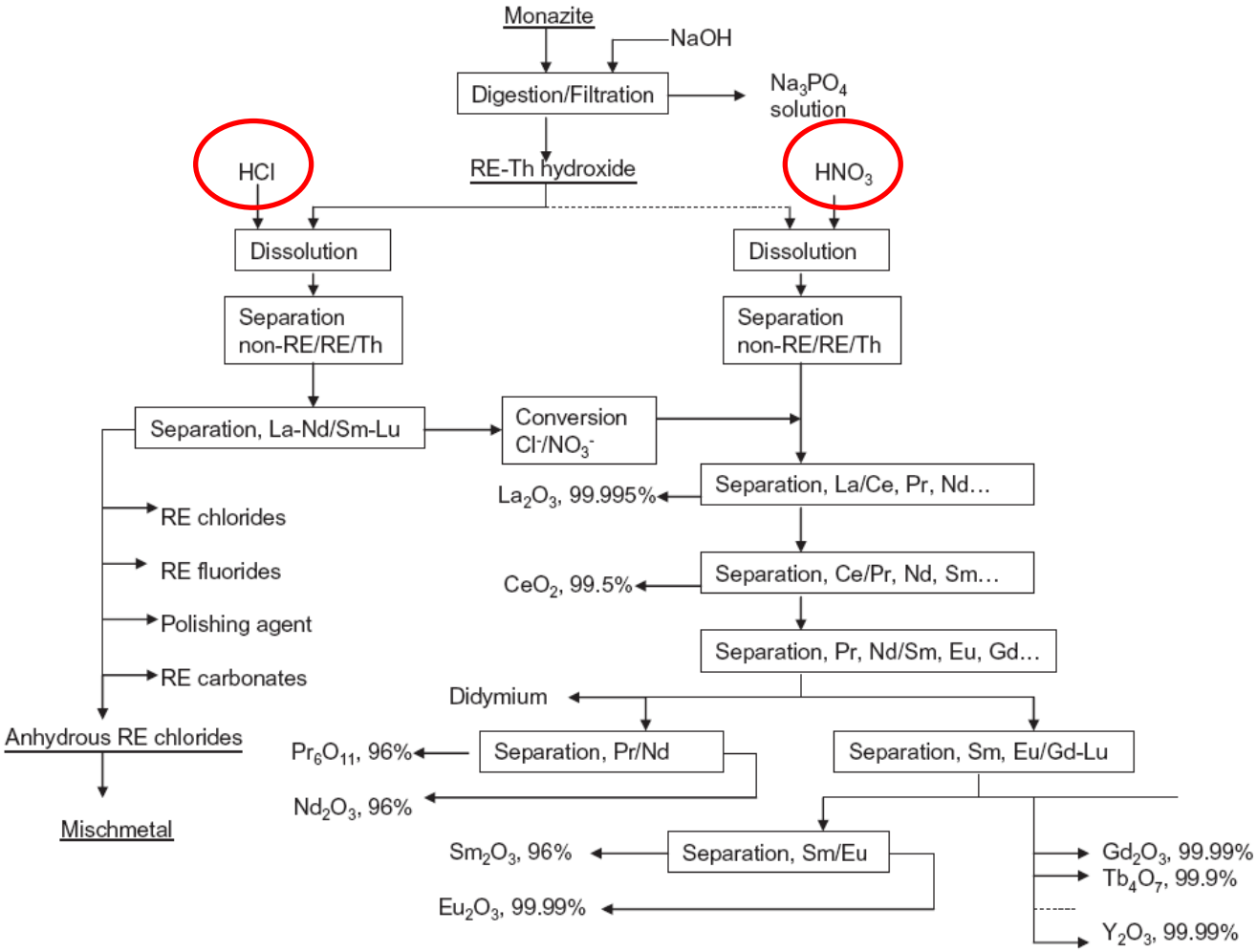
- Distribution ratio (*D*)

$$D = \frac{c_{org}}{c_{aq}}$$

- Separation factor (β or SF)

$$\beta_{A,B} = \frac{D_A}{D_B}$$

Chloride and nitrate route



Source: Xie et al., *Miner. Eng*. 56 (2014) 10-28.

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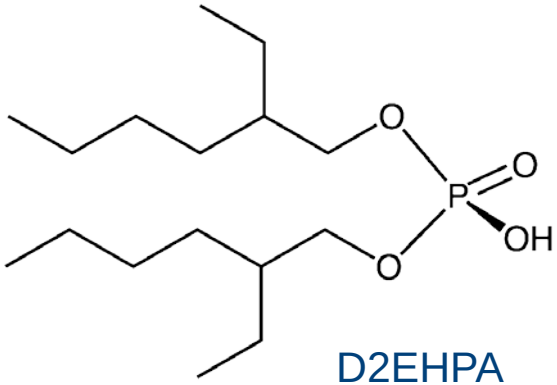
Chloride and nitrate route

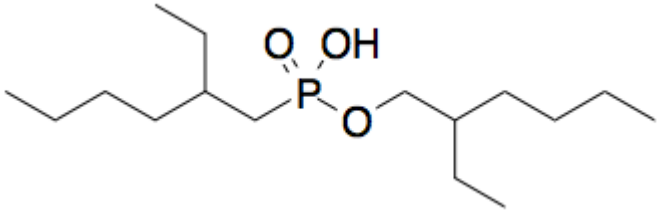
- **Chloride route**
  - \+ lower CAPEX: plastic mixer-settlers and smaller number of stages
  - \- higher OPEX: larger consumption of chemicals
    acids and bases are required for pH control and stripping
  - \- ammonium effluents to deal with
  - \- limited loading of organic phase (gel formation)
- **Nitrate route**
  - \+ lower OPEX: only water (stripping) and steam (evaporation of water to increase nitrate concentration)
  - \+ high loading of organic phase
  - \- higher CAPEX: stainless steel mixer-settlers and larger number of stages
  - \- nitrate effluents to deal with

Chloride and nitrate route

- Chloride route: acidic extractants

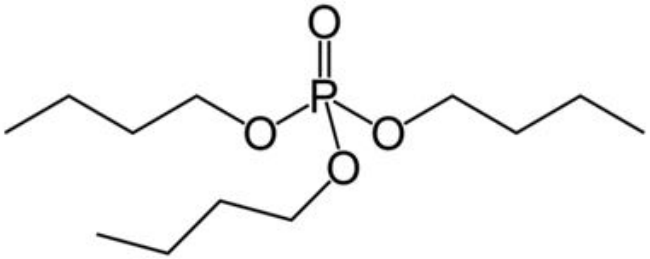


D2EHPA

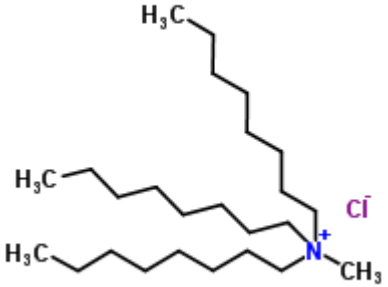


HEHEHP

- Nitrate route: neutral and basic extractants



TBP



Aliquat 336

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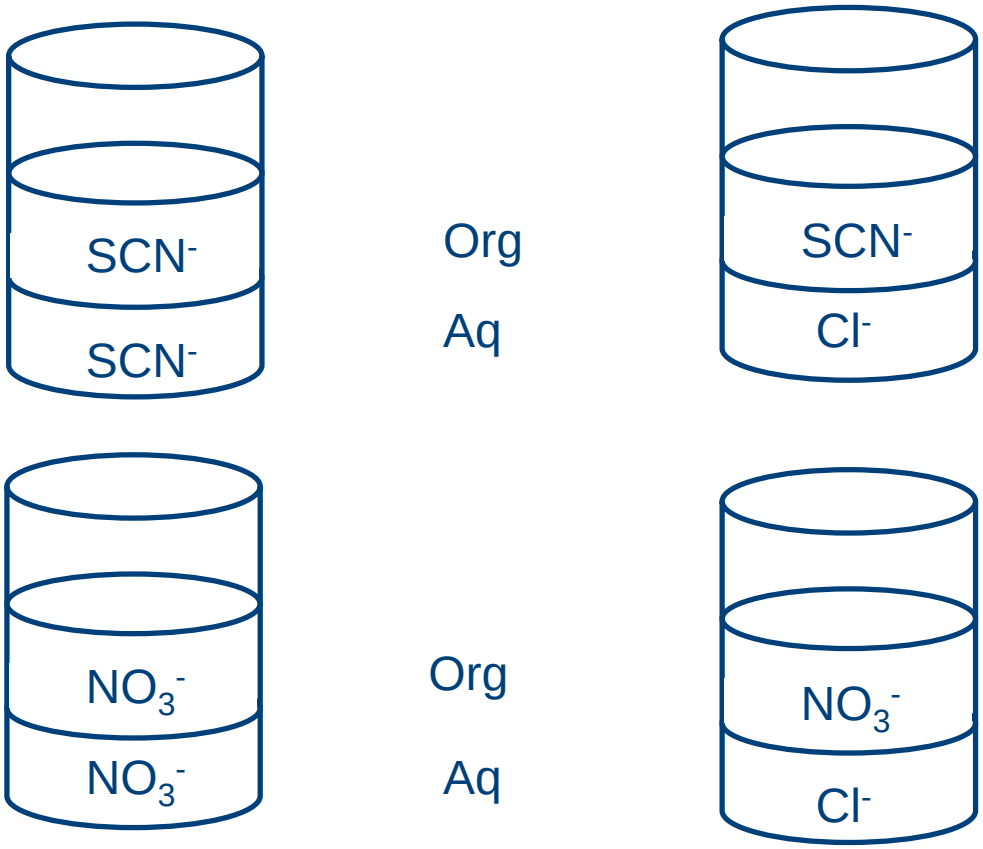
Holy Grail in REE separation

- Efficient extraction of REE from chloride solutions by neutral or basic extractants
  - High loading of organic phases (without gel formation)
  - No acids or bases consumed during separation, only water and steam
  - HCl is cheaper than HNO_3
  - No nitrate effluents
- Solution: **SPLIT-ANION EXTRACTION**

(technology invented at KU Leuven, patent application in PCT phase)

K. Larsson and K. Binnemans, *Hydrometallurgy* **156**, 206-214 (2015).

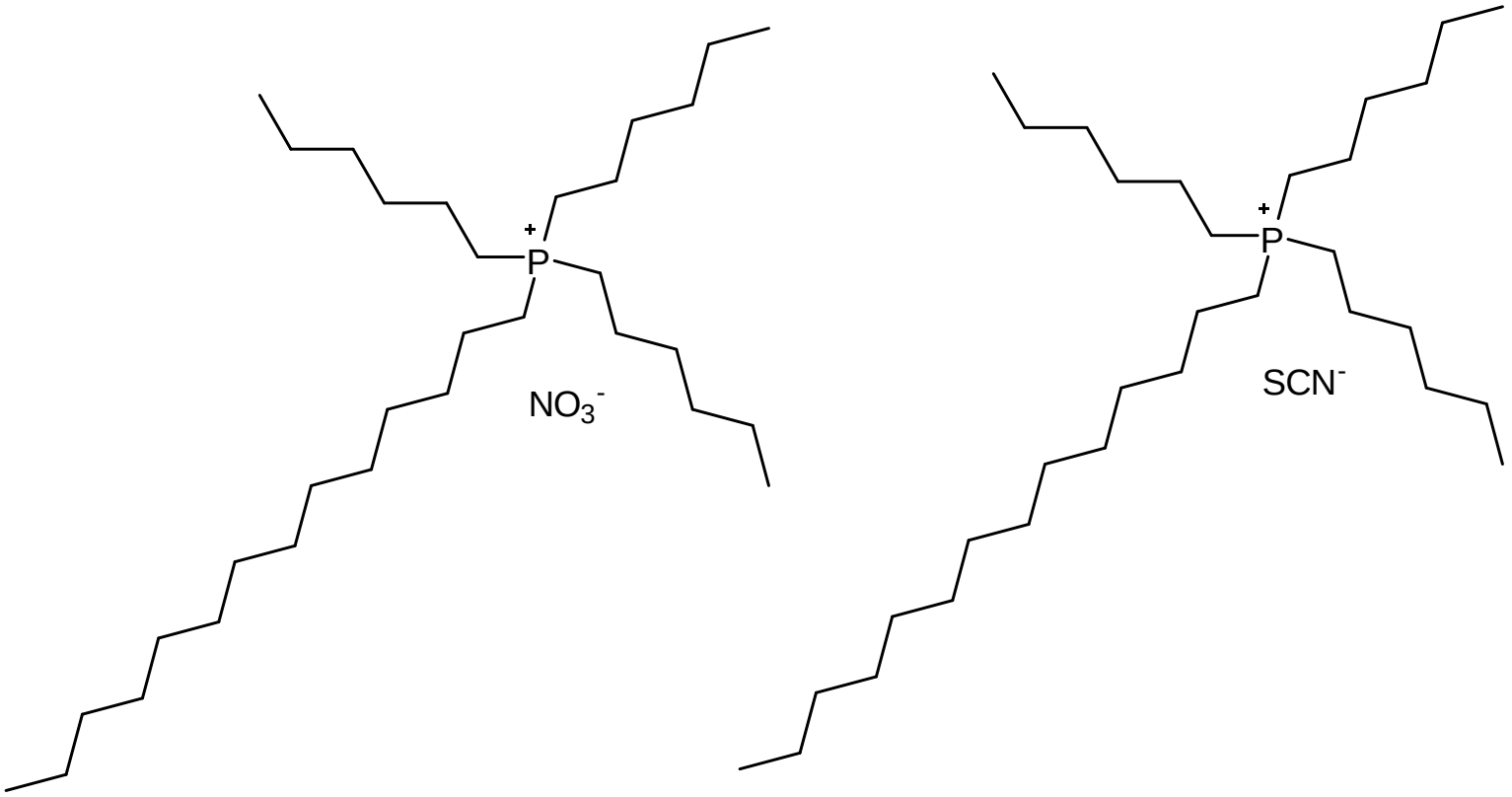
Split-anion extraction: principle



Extraction system

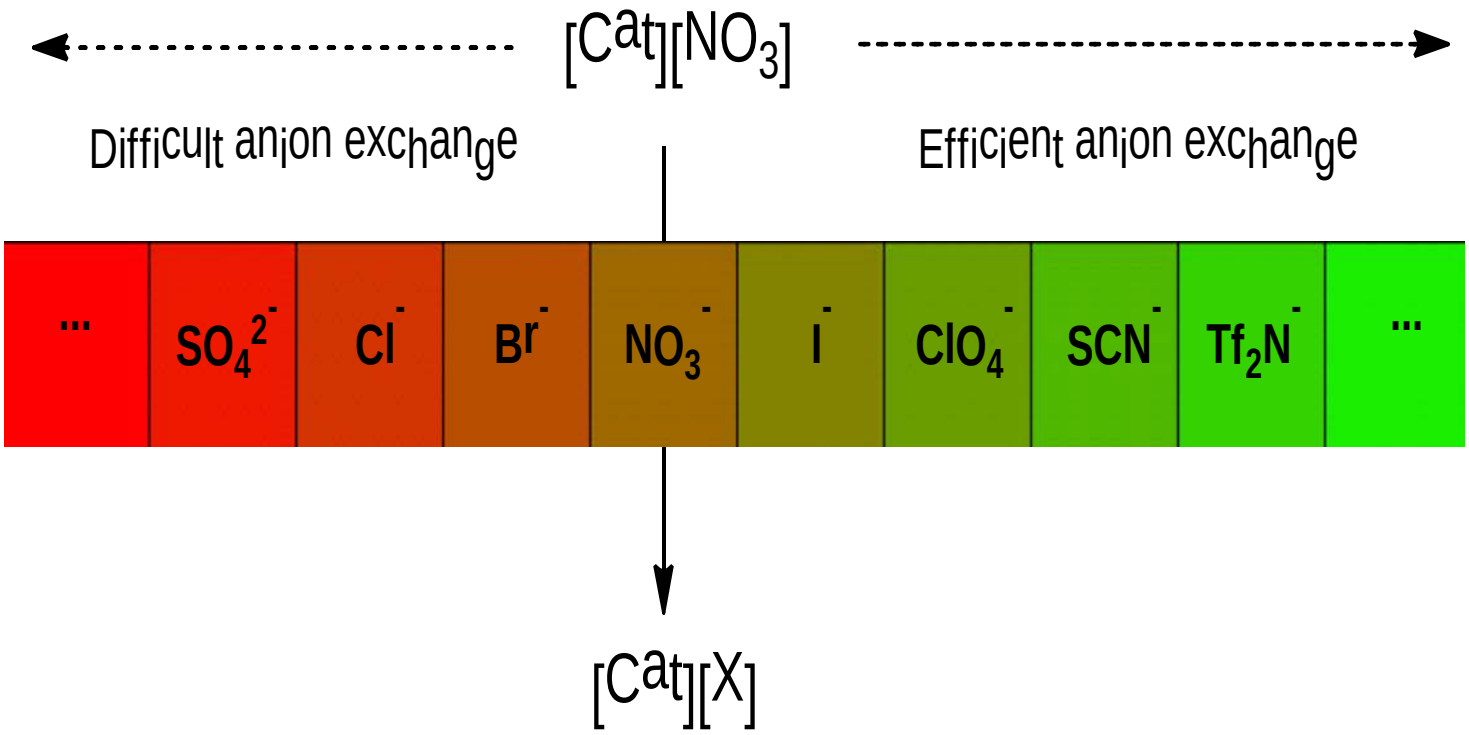
- Aqueous phase
  - rare-earth chlorides
  - with extra added chloride salts
- Organic phase
  - Pure tetraalkylphosphonium or tetraalkylammonium nitrate or thiocyanate ionic liquids
  - No molecular diluent added
- Stripping by water or by aqueous solution with low salt concentration

Ionic liquids



+ Aliquat 336 (tricaprylmethylammonium) nitrate and thiocyanate analogues

Hofmeister series



D. Dupont et al., *J. Phys. Chem. B* **119**, 6747−6757 (2015).

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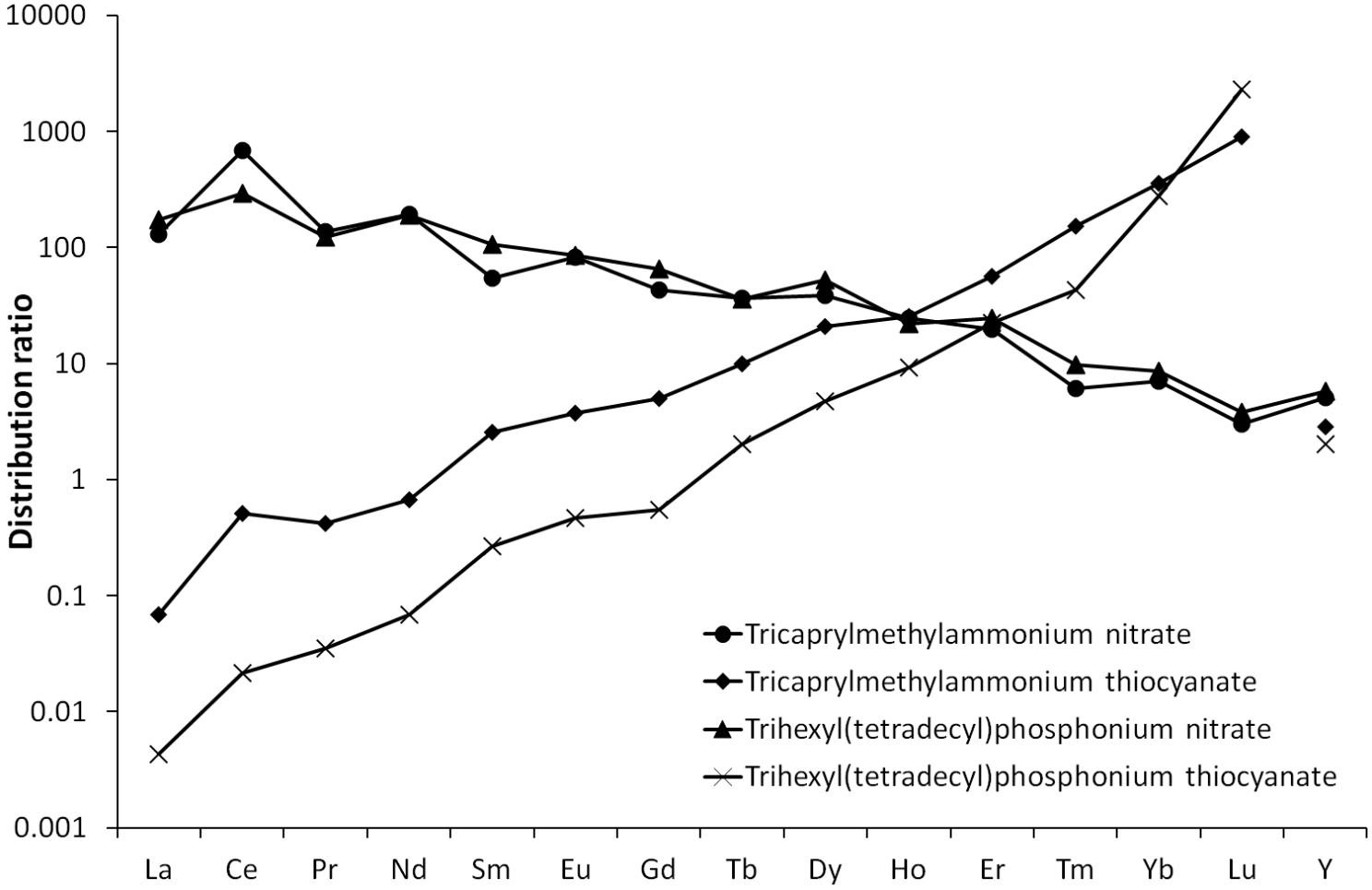
Distribution ratios



K. Larsson and K. Binnemans, *Hydrometallurgy* **156**, 206-214 (2015).

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Separation factors (SCN^-)

	Yb	Tm	Er	Ho	Dy	Tb	Y	Gd	Eu	Sm	Nd	Pr	Ce	La
Lu	8.4	54	89	100	170	650	1570	2060	1980	3000	15500	19300	38000	180000
	Yb	6.5	11	12	21	77	190	250	240	360	1850	2300	4600	21400
		Tm	1.7	1.8	3	12	29	38	37	56	290	360	700	3300
			Er	1.1	2	7	18	23	22	34	170	220	430	2000
				Ho	1.7	6.5	15.8	21	20	30	160	190	380	1800
					Dy	3.7	9.0	11.8	11	17	89	110	220	1000
						Tb	2.4	3.2	3.1	5	24	30	59	280
							Y	1.3	1.3	1.9	10	12	24	110
								Gd	1.0	1.5	7.5	9.4	19	87
									Eu	1.5	7.8	9.8	20	90
										Sm	5.1	6.4	13	59
											Nd	1.2	2.5	9.3
												Pr	2.0	9.3
													Ce	4.7

- Phosphonium thiocyanate
  - Loading dependent (here only ~15g/L)
  - Much higher loadings are possible

K. Larsson and K. Binnemans, *Hydrometallurgy* **156**, 206-214 (2015).

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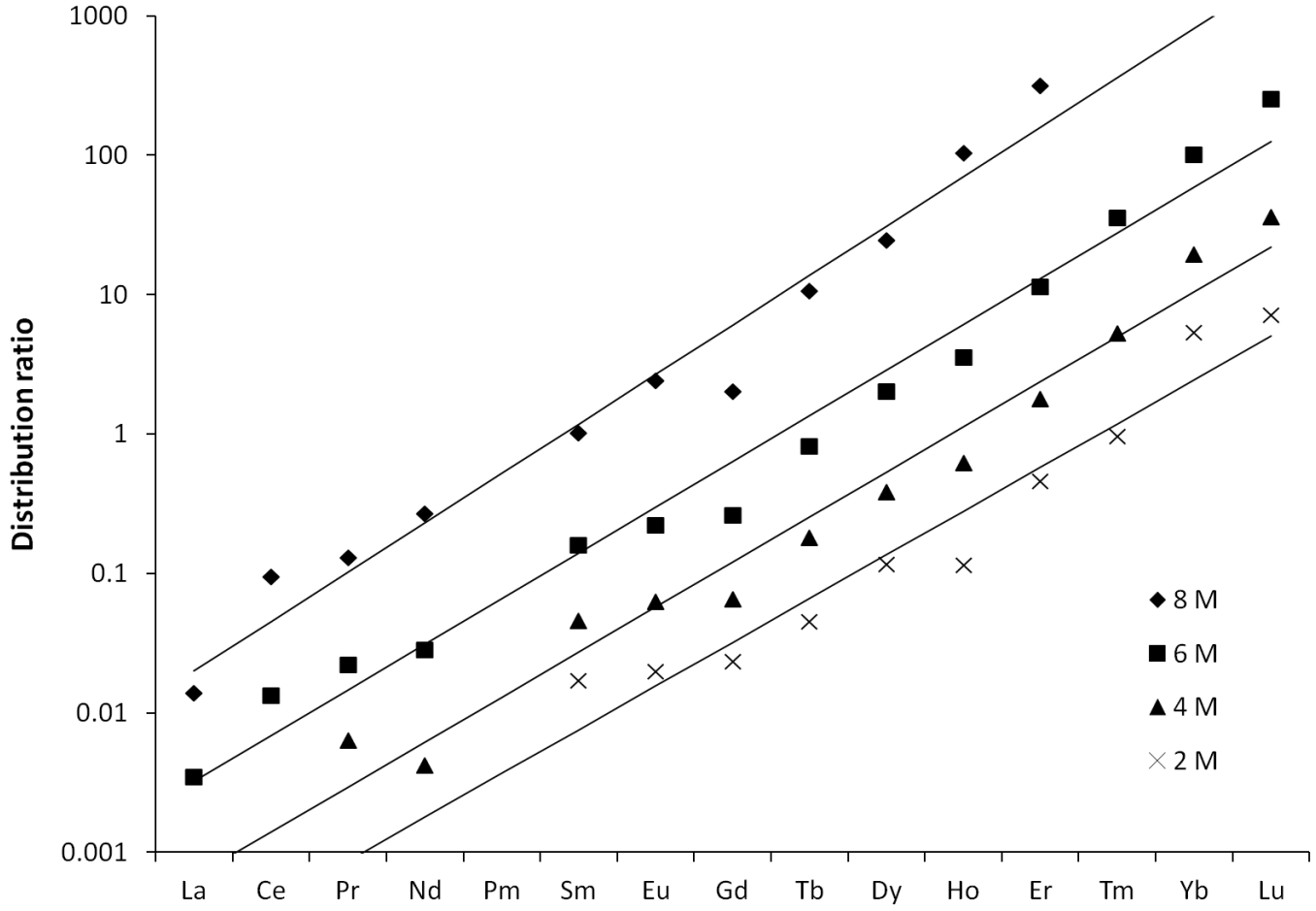
Influence of [Cl^-]



K. Larsson and K. Binnemans, *Hydrometallurgy* **156**, 206-214 (2015).

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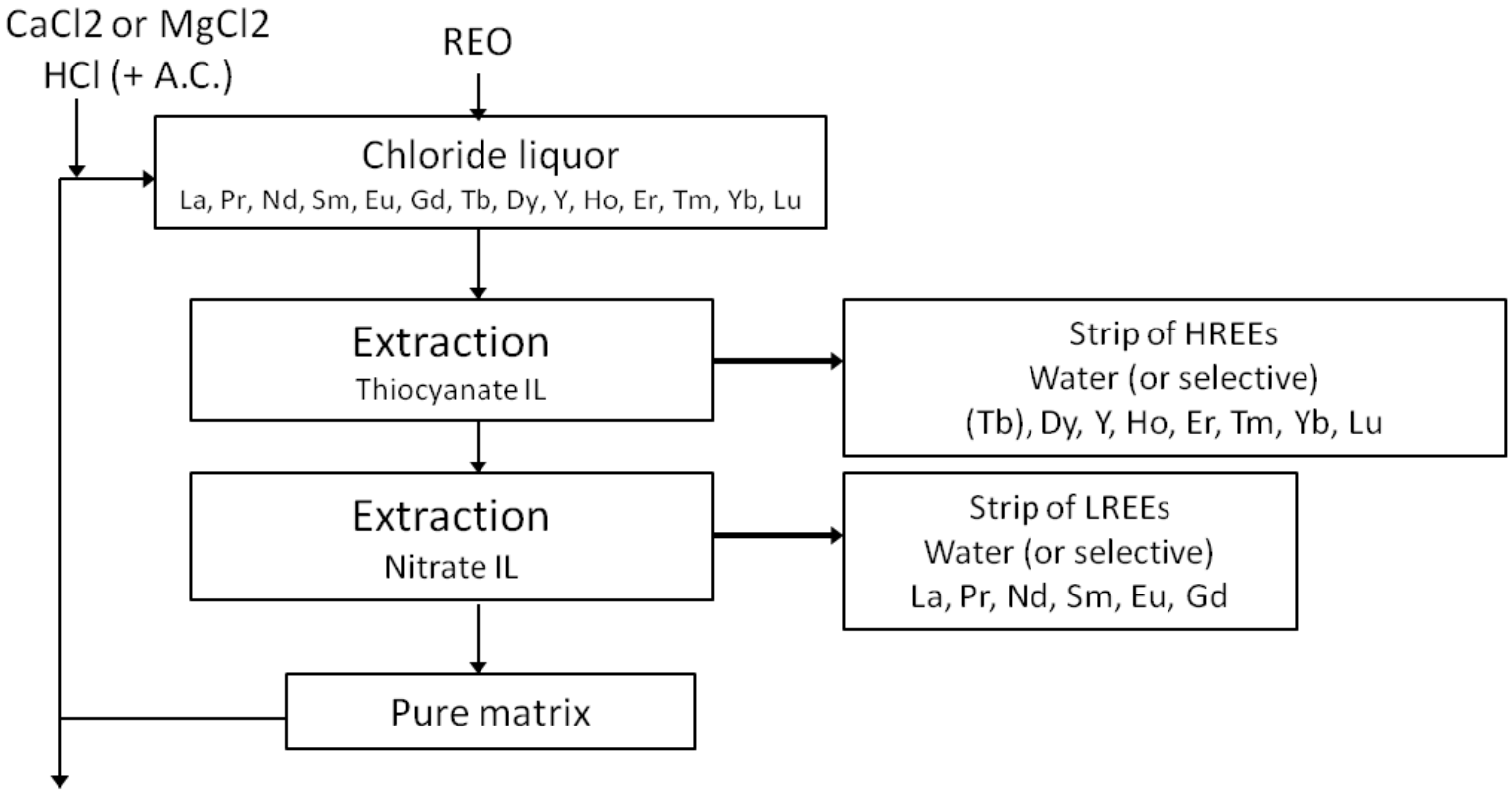
Simplified flowsheet



K. Larsson and K. Binnemans, *Hydrometallurgy* **156**, 206-214 (2015).

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REE recycling from permanent magnets

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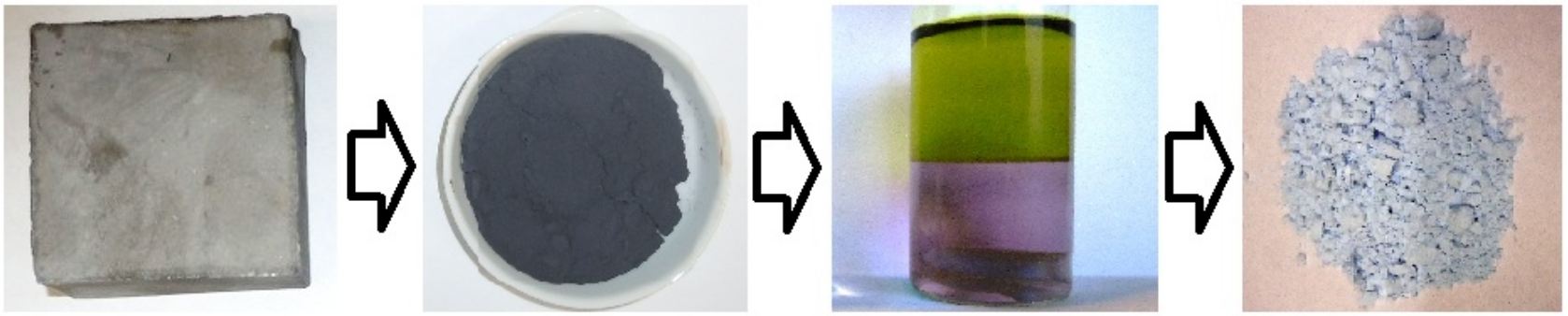
SmCo and NdFeB magnets

- **samarium-cobalt alloys** (SmCo): $SmCo_5$ and Sm_2Co_{17}
  - maximum energy product $(BH)_{max}$:130 to 260 kJ/m^3
  - good corrosion resistance
  - high operating temperatures
  - expensive (Co)
  - small part of REE magnet market (2-5%): niche applications
- **neodymium-iron-boron alloy** (NdFeB): $Nd_2Fe_{14}B$
  - maximum energy product $(BH)_{max}$:512 kJ/m^3
  - poor corrosion resistance (surface plating required)
  - lower operating temperatures (Dy addition)

Recovery of REE from magnets

- Steps:
  - Milling and roasting
  - Dissolution or selective leaching (HCl)
  - Removal of transition metals by solvent extraction (with ionic liquids)
  - Precipitation of REEs (oxalate) and calcination to oxide



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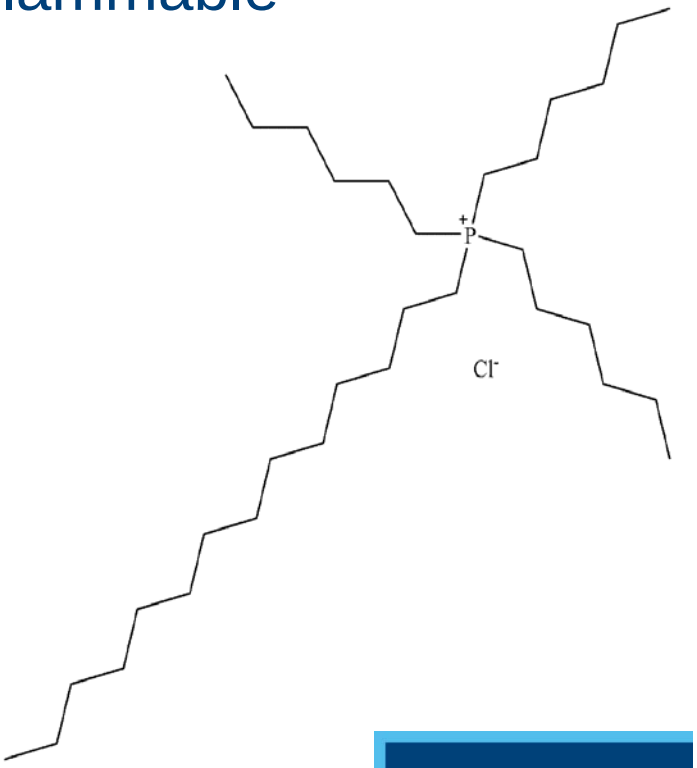
Solvent extraction with $[P_{66614}][Cl]$

- Ionic liquid: trihexyl(tetradecyl)phosphonium chloride $[P_{66614}][Cl]$ (Cyphos IL 101)
  - Negligible vapor pressure, non-flammable
  - Non-fluorinated
  - Undiluted
  - Cl^- can be replaced by NO_3^- by anion exchange



T. Vander Hoogerstraete et al., *Green Chemistry* **15**, 919-927 (2013).

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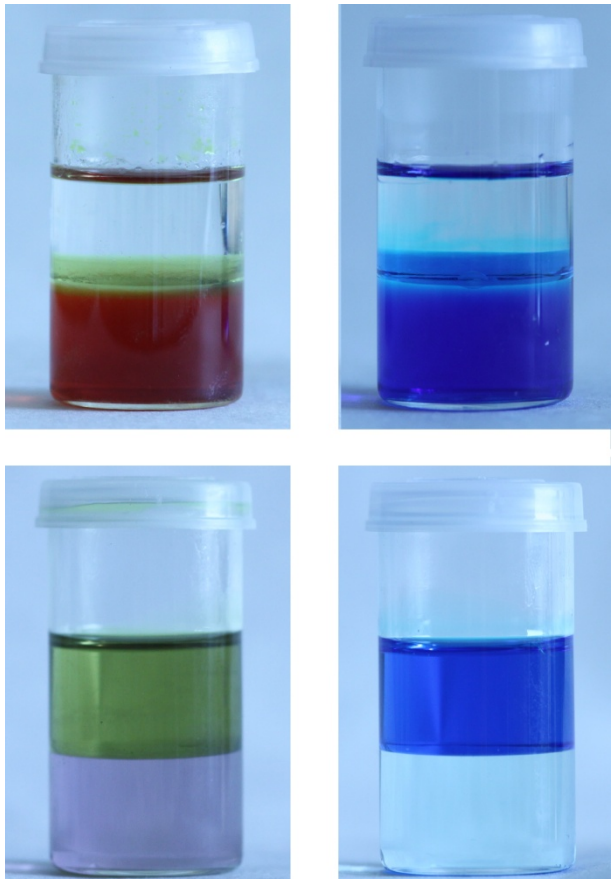
Selectivity by choice of IL anion

- $[P_{66614}][Cl]$
  - Transition metals extracted to organic phase
  - REE left behind in raffinate
- $[P_{66614}][NO_3]$
  - REE extracted to organic phase
  - Many transition metals left behind in raffinate

Solvent extraction with Cyphos IL 101

- Extractions tested for Nd/Fe and Sm/Co separations
- Fe and Co are extracted
- Rare earths not extracted and remain in water phase
- Separation factors:

  Nd/Fe or Sm/Co > 10^6



T. Vander Hoogerstraete et al., *Green Chemistry* **15**, 919-927 (2013).

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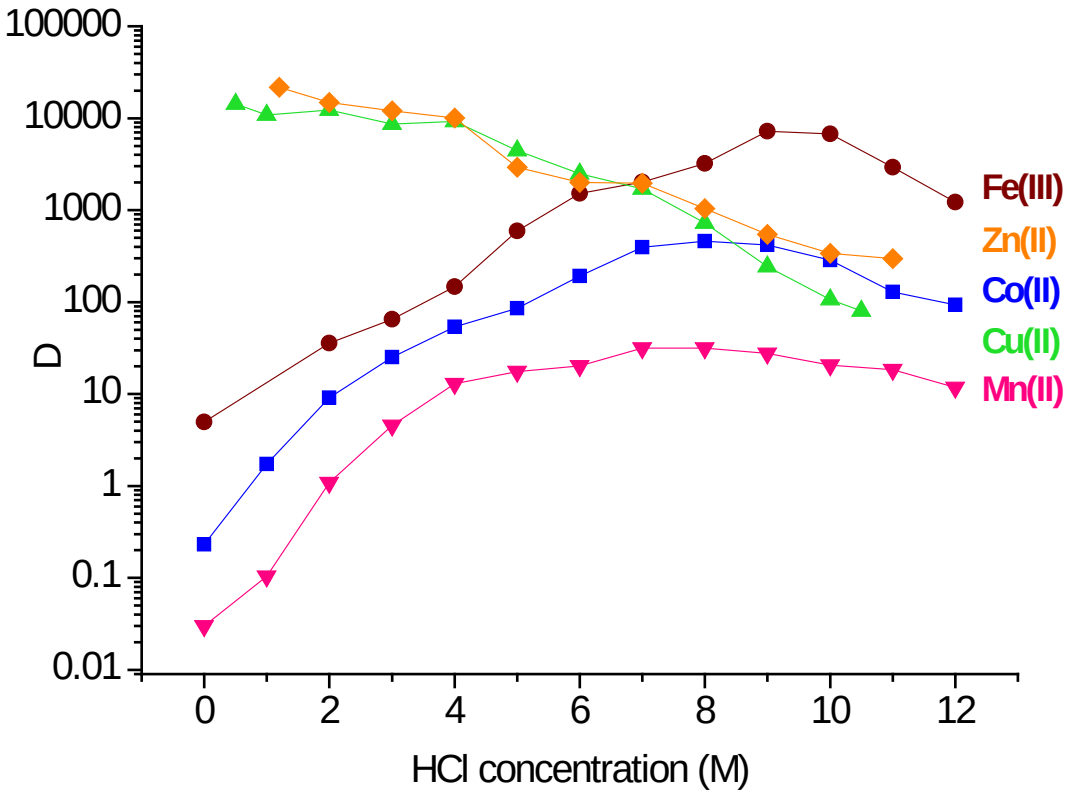
Extraction with $[P_{66614}][Cl]$



Ref.: T. Vander Hoogerstraete et al., *Green Chemistry* **15**, 919-927 (2013).

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Extraction with $[P_{66614}][NO_3]$

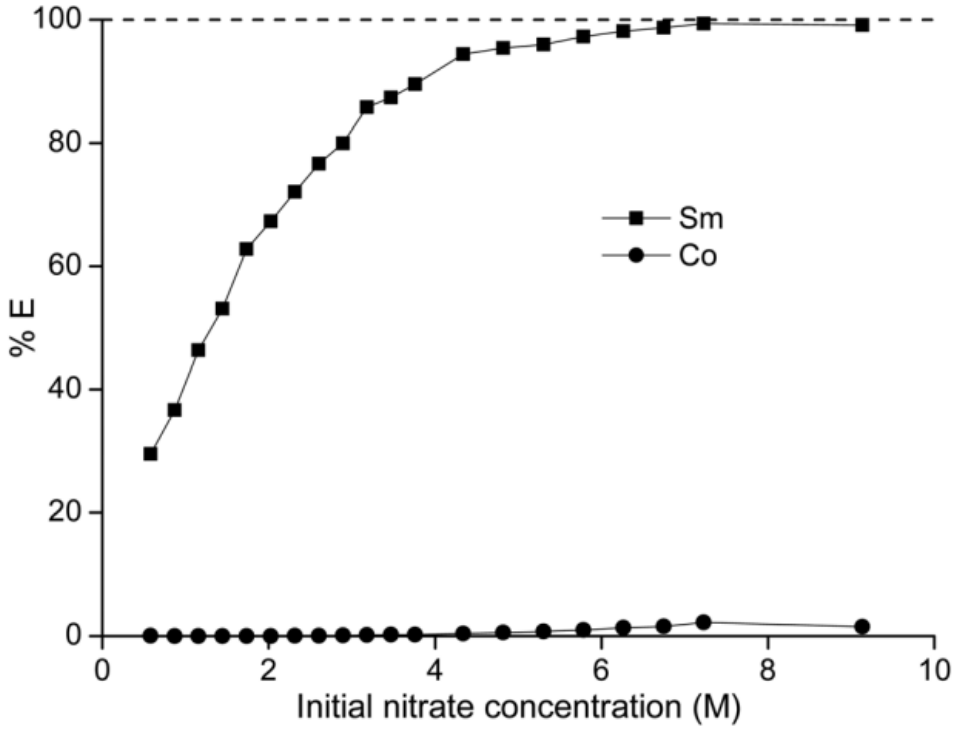

Fig. 1 Percentage extraction (%*E*) of samarium (■) and cobalt (●) as a function of the initial nitrate concentration in the aqueous phase.

T. Vander Hoogerstraete and K. Binnemans, *Green Chemistry* **16**, 1594-1606 (2014).

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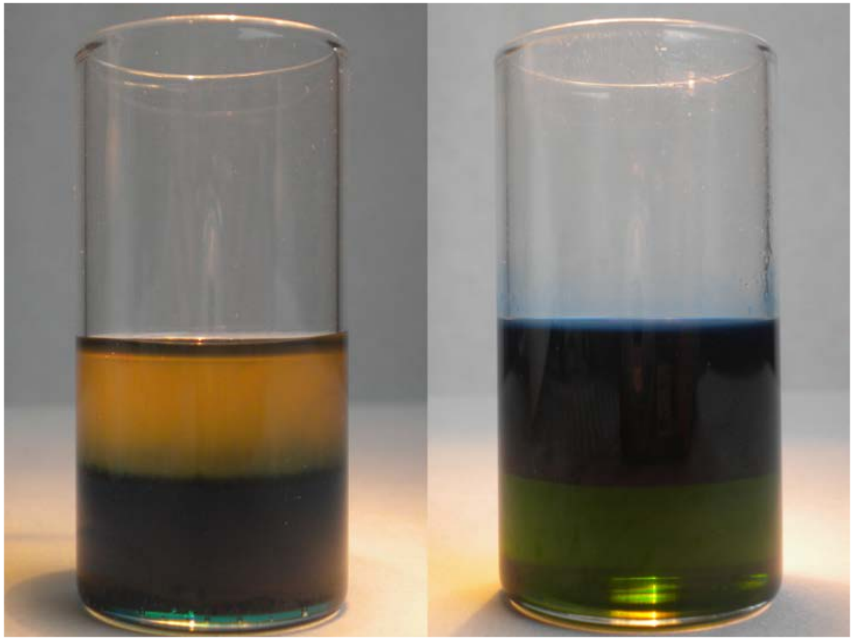
IL-IL extraction



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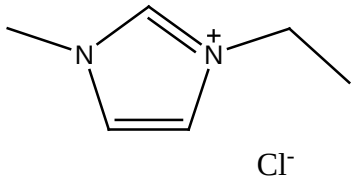
IL-IL extraction

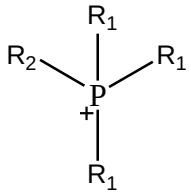
- Coordinating ionic liquids (metal complex formation)
  - Dissolution of metal ions
- A hydrophilic ionic liquid

  1-Ethyl-3-methylimidazolium chloride (EmimCl)



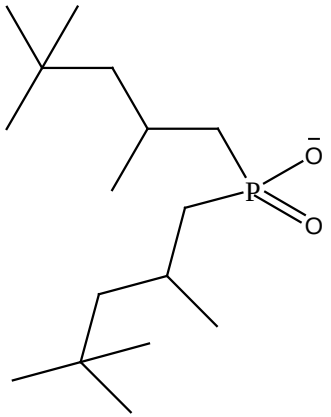
- A hydrophobic ionic liquid

  Tri(hexyl)tetradecylphosphonium bis-[2,4,4-trimethyl(pentyl)]phosphinate ($P_{66614}R_2POO$)



R_1= hexyl

R_2= tetradecyl



S. Wellens, B. Thijs, C. Möller, and K. Binnemans, *Phys. Chem. Chem. Phys.*, 2013, **15**, 9663-9669.

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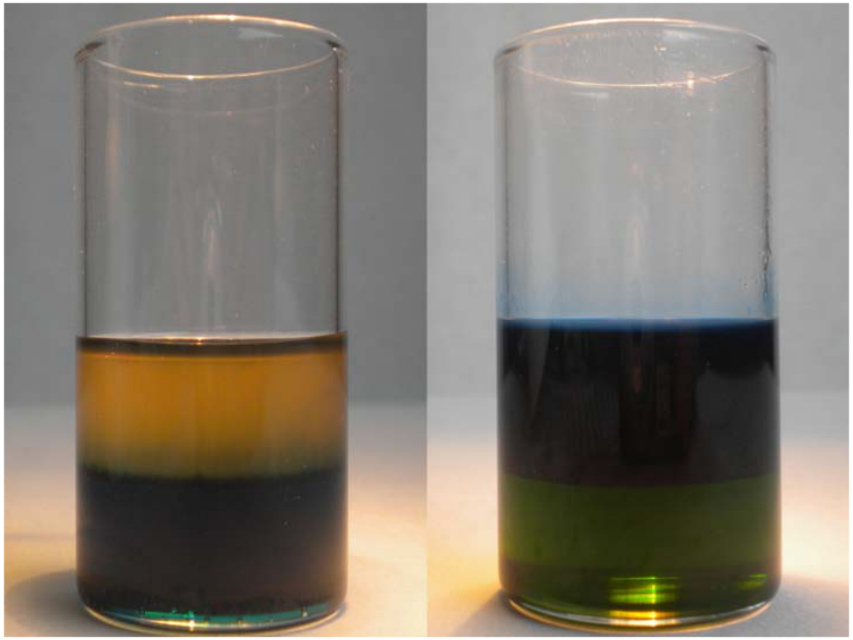
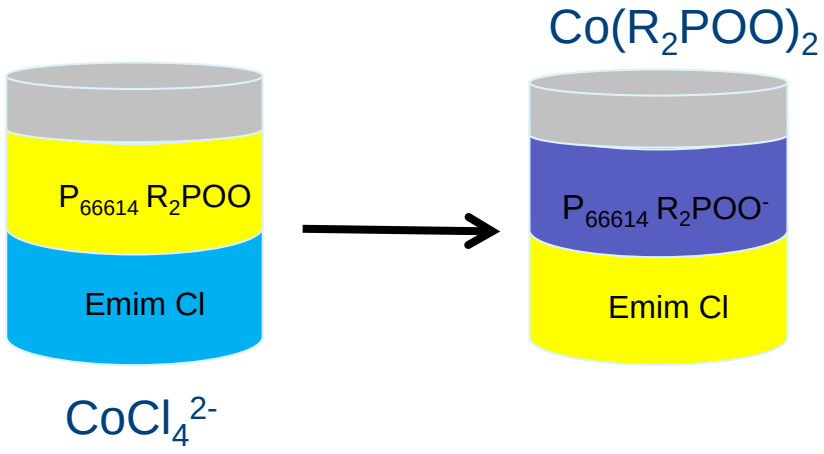
IL-IL extraction

- Dissolution of $CoCl_2$ in EmimCl phase
- Extraction to $P_{66614}R_2POO$ phase



$$D_{Co} = \frac{[Co]_{P_{66614}R_2POO}}{[Co]_{EmimCl}} = 44$$



S. Wellens, B. Thijs, C. Möller, and K. Binnemans, *Phys. Chem. Chem. Phys.*, 2013, **15**, 9663-9669.

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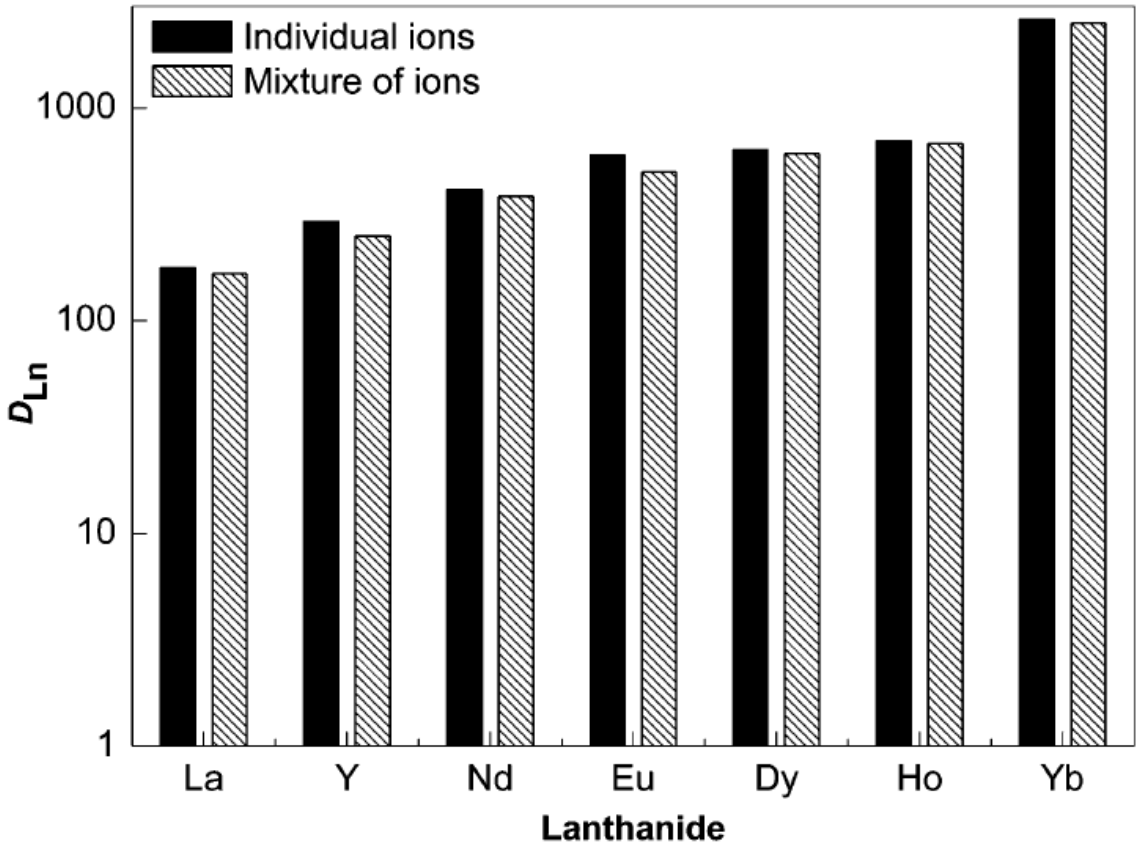
IL-IL extraction



A. Rout et al., *RSC Advances* **4**, 5753–5758 (2014)..

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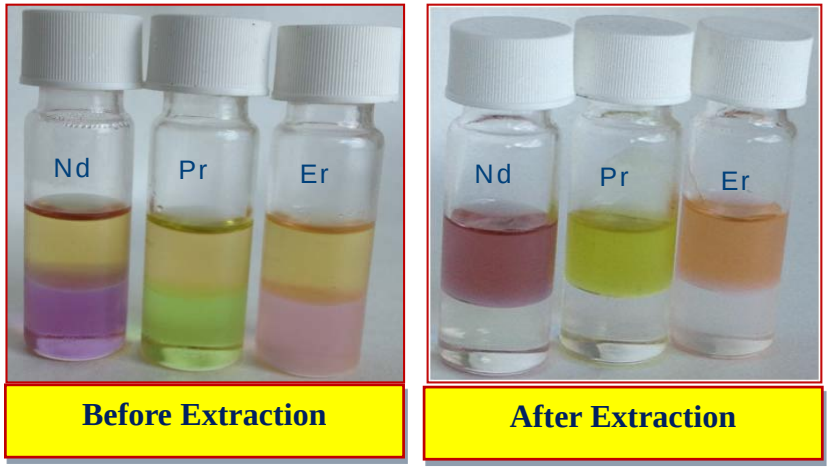
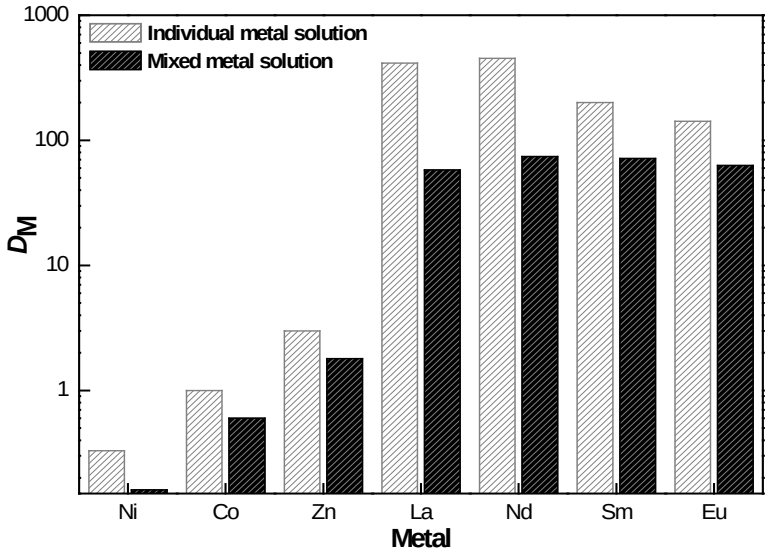
IL-IL extraction

- Dissolution of $RE(NO_3)_3 \cdot xH_2O$ in $Ca(NO_3)_2 \cdot 4H_2O$ phase *molten salt hydrate* → no free water molecules
- Extraction to $[A336][NO_3]$ phase at 53 °C





A.Rout and K. Binnemans, *Dalton Transactions* **43**, 3186-3195 (2014).

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REE recycling from fluorescent lamps

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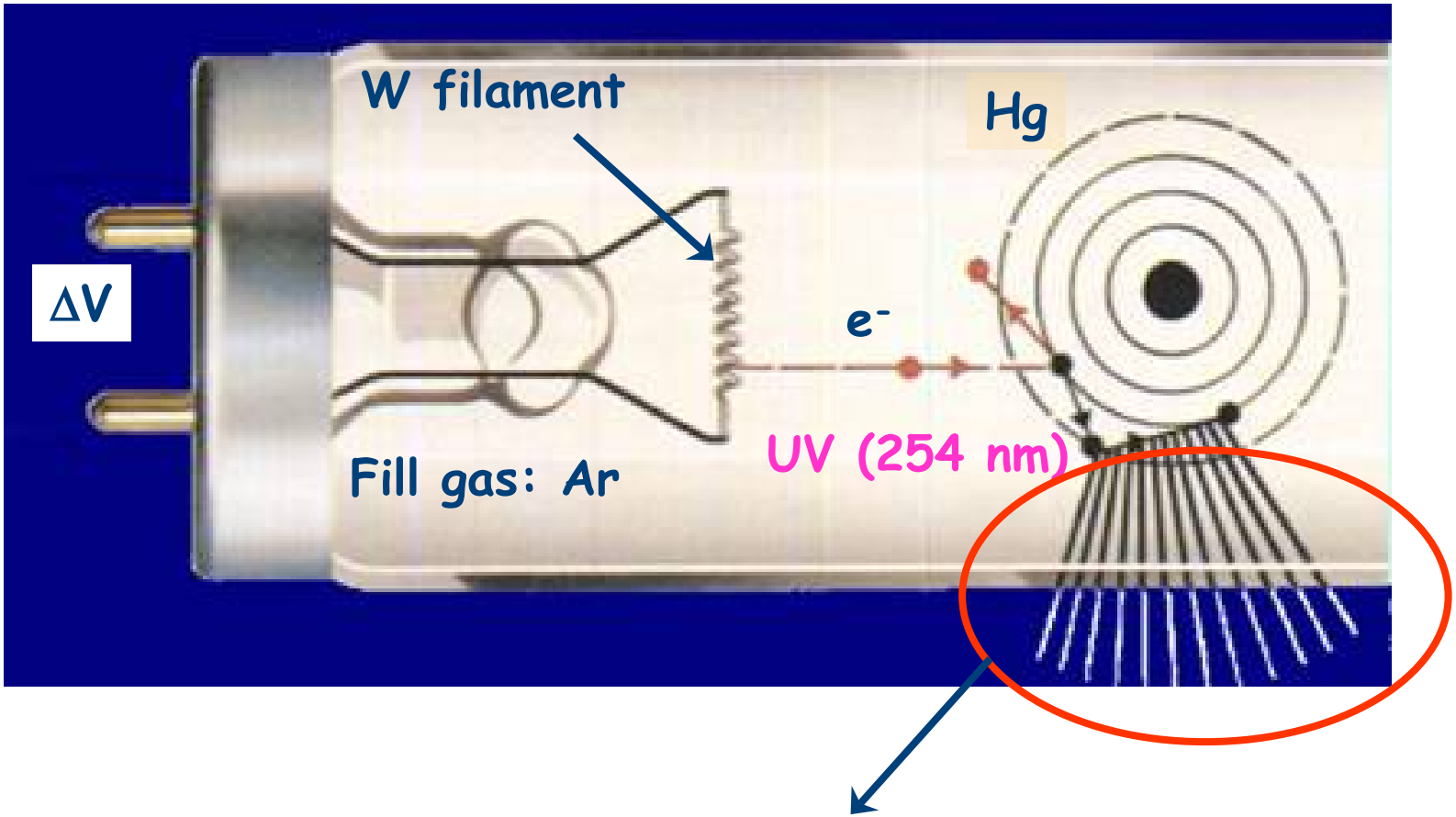
Fluorescent lamps



UV photons excite phosphor coating. White light is emitted.

Lamp phosphors

Year	Phosphors		
1960	$Ca_5(PO_4)_3Cl:Sb^{3+},Mn^{2+}$ (white)		
1974	$BaMg_2Al_{16}O_{27}:Eu^{2+}$	$CeMgAl_{10}O_{19}:Tb^{3+}$	$Y_2O_3:Eu^{3+}$ (YOX)
1990	$BaMgAl_{10}O_{17}:Eu^{2+}$ $(Sr,Ca)_5(PO_4)_3Cl:Eu^{2+}$	$(La,Ce)PO_4:Tb^{3+}$ $CeMgAl_{10}O_{19}:Tb^{3+}$ $(Gd,Ce)MgB_5O_{10}:Tb^{3+}$	$Y_2O_3:Eu^{3+}$ (YOX)
2005	$BaMgAl_{10}O_{17}:Eu^{2+}$	$(La,Ce)PO_4:Tb^{3+}$	$Y_2O_3:Eu^{3+}$ (YOX)

Different options for recycling of lamp phosphors

- Direct re-use
- Separation of phosphors in individual components
- **Recovery of REE content**

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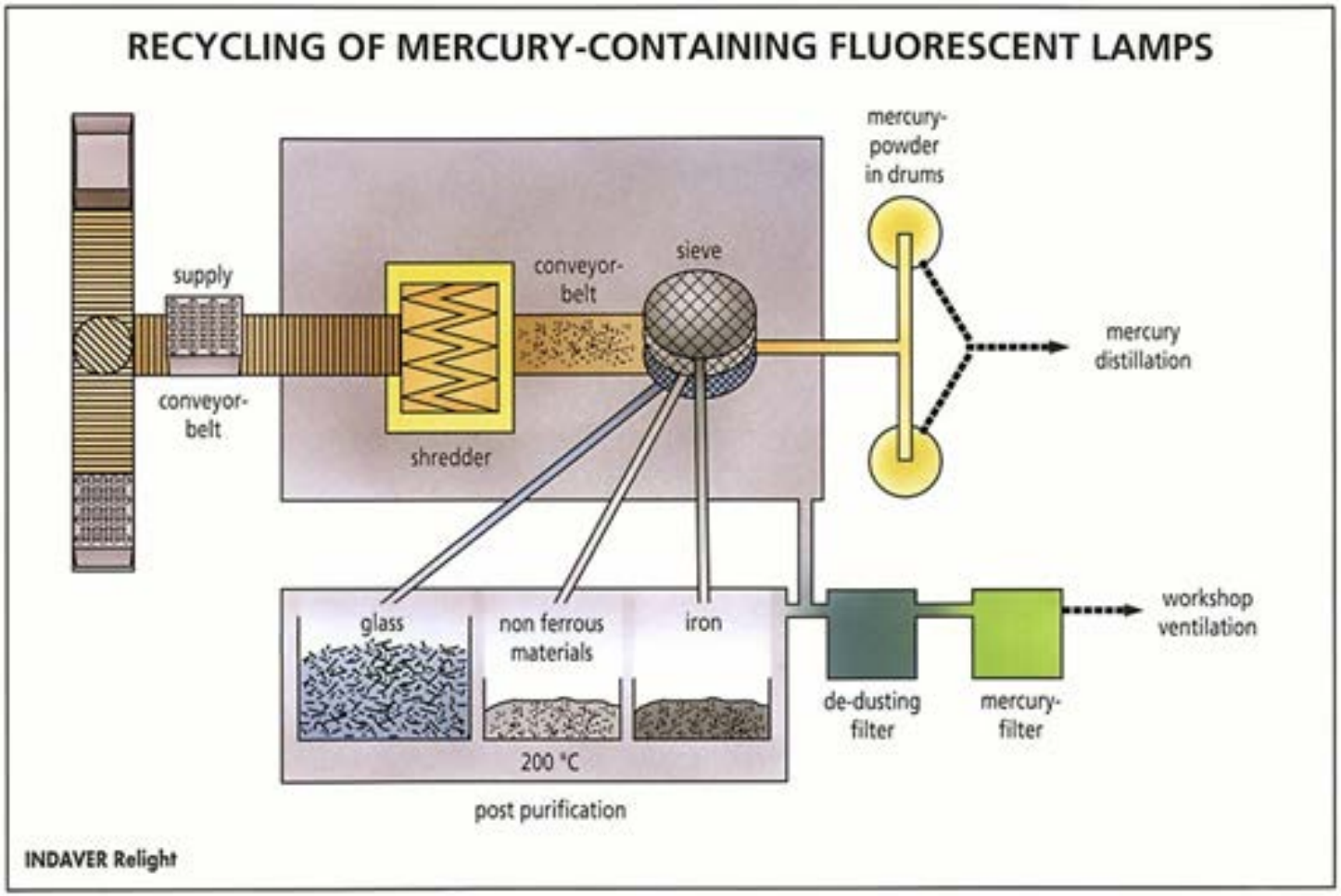
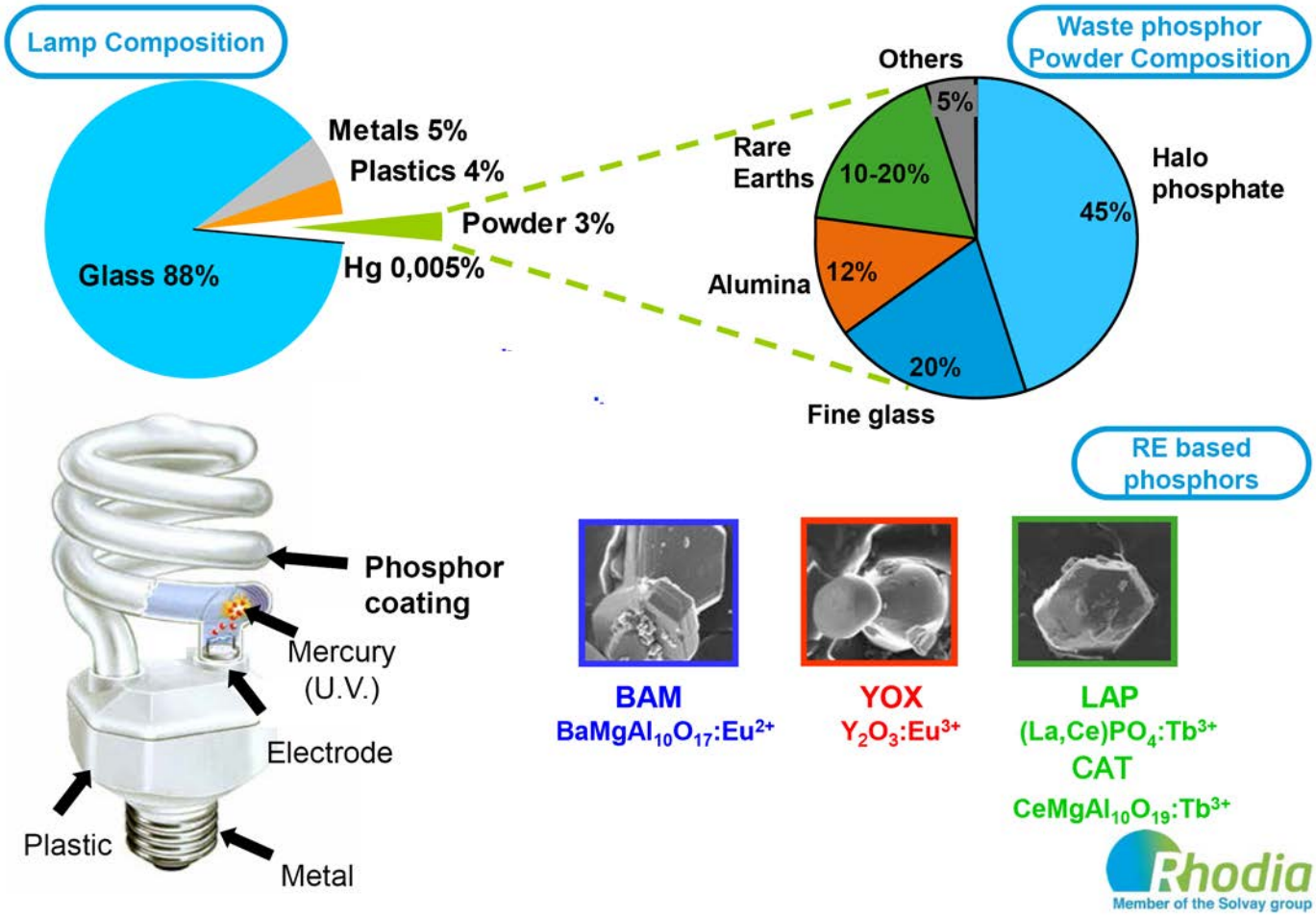
Crushing and sieving of fluorescent lamps



Lamp phosphors



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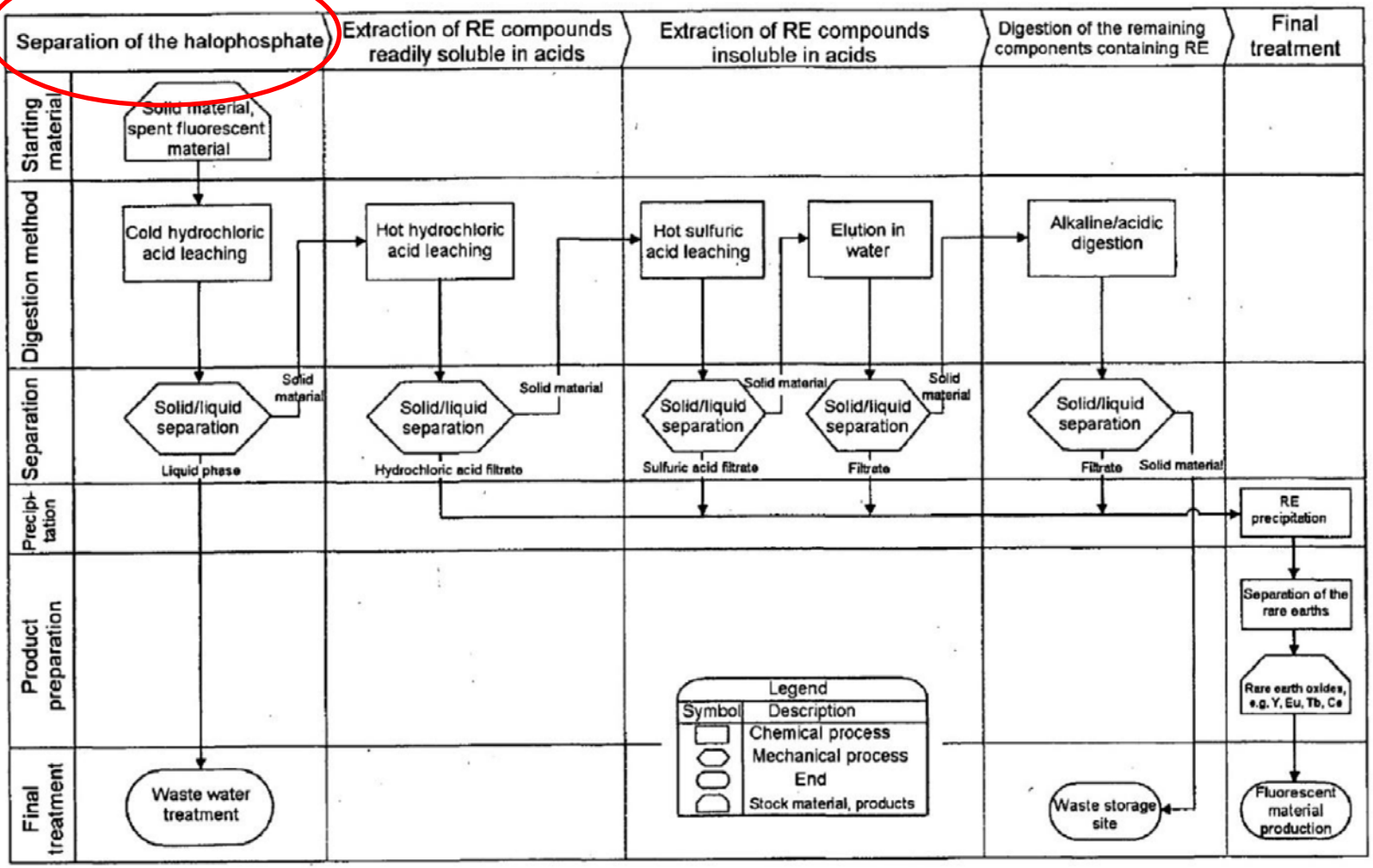

Otto, R., Wojtalewicz-Kasprzac, A., 2012. Method for Recovery of Rare Earths From Fluorescent Lamps. US Patent 2012/0027651 A1

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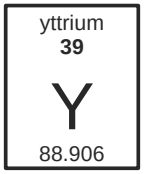
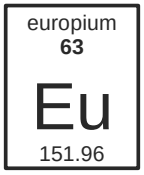
KU Leuven process





- New recycling process for lamp phosphor waste
- Selective dissolution of the red phoshor YOX

  Immediate regeneration of high-quality YOX
- No need for solvent extraction
- Green, ionic liquid technology

  (low waste and energy)

Selective dissolution of YOX is impossible in aqueous solutions because the halophosphate (50 wt% of the waste) will always dissolve prior to YOX.

D. Dupont and K. Binnemans, *Green Chemistry* **17**, 856–868 (2015).
Patent application filed

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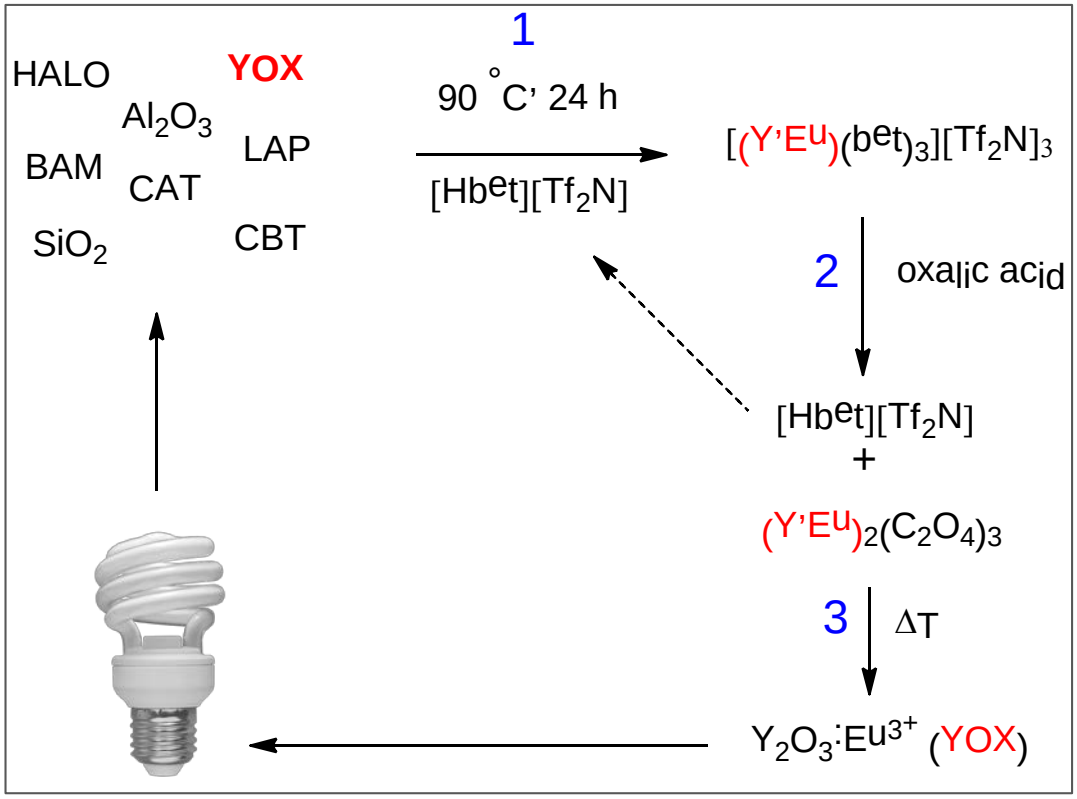
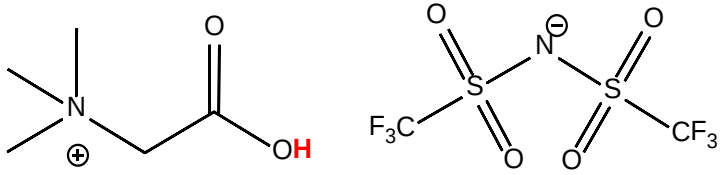
Process flowsheet





[Hbet][Tf_2N]

Process Overview

1. Selective dissolution of YOX
   no dissolution of halophosphate
2. Stripping with oxalic acid
3. Direct resynthesis of YOX

D. Dupont and K. Binnemans, *Green Chemistry* **17**, 856–868 (2015).

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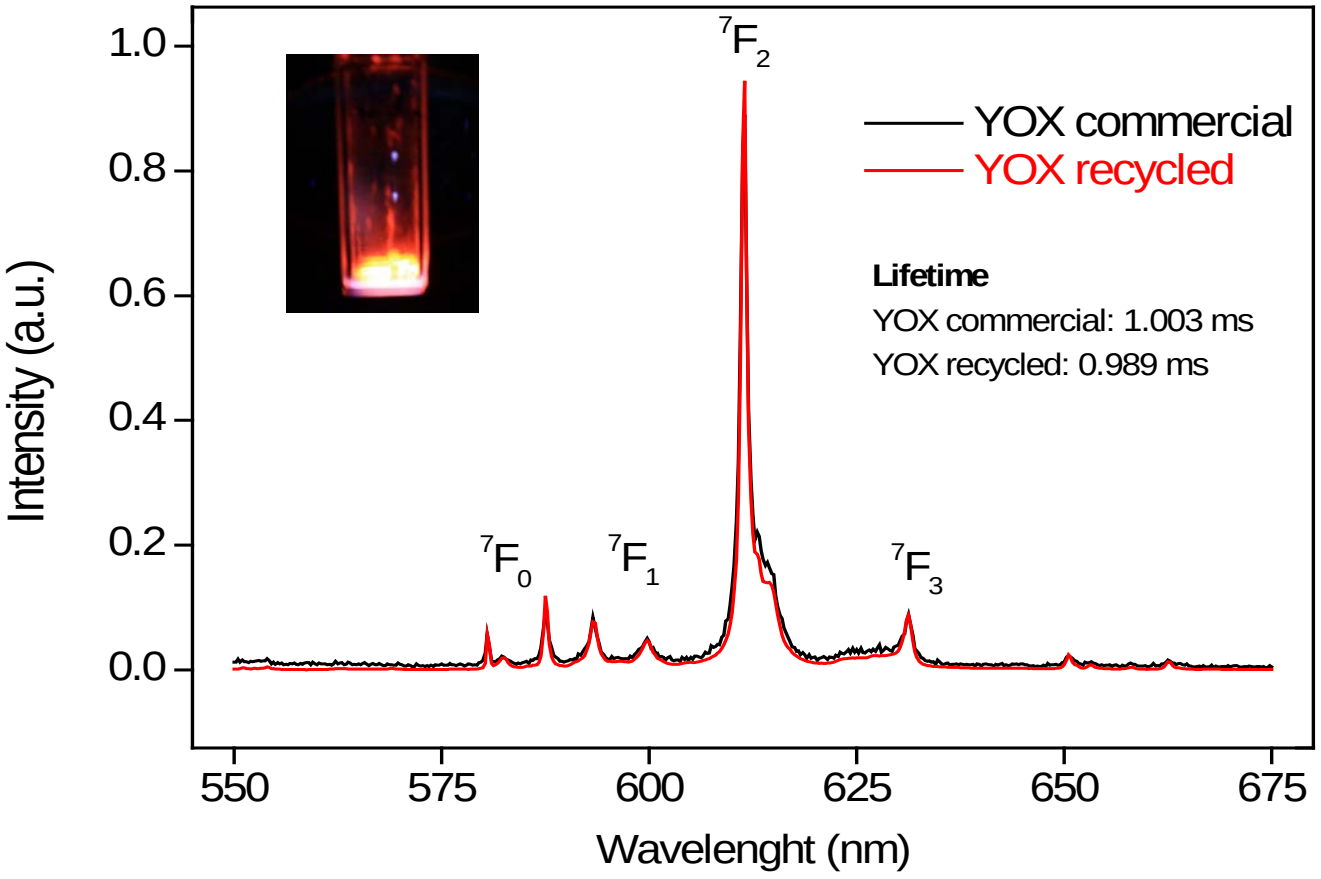
New versus recycled YOX



D. Dupont and K. Binnemans, *Green Chemistry* **17**, 856–868 (2015).

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Conclusions

- Solvent extraction with undiluted ionic liquids
- Separation of rare-earths by split-anion extraction
- IL process for REE recovery from NdFeB and SmCo magnets
- IL-IL extraction with mutually immiscible ionic liquids
- IL process for recycling of red lamp phosphor $Y_2O_3:Eu^{3+}$

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Thank you !

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